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Polycarbonate (PC)

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INTRODUCTION

Polycarbonate (PC), with its unique combination of toughness, transparency, processability, and temperature resistance, is one of the most important engineering thermoplastics in the world today. It is found in a wide range of products, from CDs and DVDs to greenhouses and optical lenses to automotive lighting and instrument panels. Polycarbonate forms a number of useful blends and composites and can be produced in a wide range of transparent and opaque colors, making it the material of choice for many products with special visual effects, like specially colored computer housings and personal communication devices. Bisphenol A polycarbonate (BPA-PC) is the most important commercial PC and is the primary subject of this review. Until recently, BPA-PC was produced via an interfacial polymerization process. Recently commercialized melt processes provide solvent- and phosgene-free production routes. This article provides a brief summary of the historical development of BPA-PC, an overview of commercial products and producers, a review of PC physical and mechanical properties, a description of current commercial production processes for PC as well as new process developments, an overview of processing and fabrication processes employed with PC, a summary of PC blends, copolymers, and applications, and a summary of PC literature.

BACKGROUND AND HISTORY

Interest in PC continues to grow, with over 44,000 current publications and patents, of which some 55% are patents.^[1] Before 1960, there were fewer than 100 total publications and patents on PC. Annual new publications increased from around 200 per year in the 1960s to 2000 per year in the 1990s, with continued growth of approximately 1400 new patents published per year since 2000. Similarly, global production and consumption of PC continue to grow, with an estimated 1.5 million metric tons of global consumption in 2000^[2] and a projected annual growth rate of 7% per year.^[3] GE has the largest global market share of PC resin (sold under the trademark LEXAN[®] resin),^[4,5]

with Bayer (Makrolon[®])^[6] holding second place. Other major global producers of PC resin include Dow Chemical Company (CALIBRE[®]),^[7] Teijin (Panlite[®]),^[8] and Mitsubishi Engineering Plastics Corporation (Iupilon[®]).^[9] There are frequent announcements of expansions, licenses, and plans for new production sites to serve emerging markets around the world.^[10–12]

Polycarbonate based on 2,2-bis(4-hydroxyphenyl)propane (bisphenol A, BPA) is the PC of primary commercial interest (Fig. 1), but commercial production of BPA-PC did not begin until the 1960s.^[13] The earliest reports of aromatic PC preparation, by Einhorn, appeared in the late 1800s and involved reaction of hydroquinone or resorcinol with phosgene in pyridine solution.^[14] In 1902, Bischoff and Hedenstroem^[15] reported a melt synthesis of these polymers via transesterification with diphenyl carbonate. Carothers and Van Natta^[16] reported aliphatic PC synthesis in the 1930s. Aliphatic PCs display low melting points, strength, and durability and are generally of little commercial interest. The first commercial PC material, a cross-linkable allyl diglycol carbonate (CR-39[®]), was introduced by Pittsburgh Plate Glass Company (PPG) in the 1940s.^[17]

Researchers at GE and Bayer independently developed commercially feasible synthetic processes for BPA-PC in the 1950s^[18,19] and began commercial production in the early 1960s. Bayer was awarded the U.S. patent for PC produced via the interfacial polymerization process^[20] and GE the U.S. patent for the melt transesterification process.^[21] However, until recently, the major part of BPA-PC was produced via the interfacial process. Further information on the history of PC development can be found in previously published reviews.^[22–28]

POLYCARBONATE STRUCTURE AND PROPERTIES

Aromatic PC based on BPA (Fig. 1) is the most important commercial PC. BPA-PC is amorphous and transparent, with a glass transition temperature (T_g) of approximately 150°C. The high T_g of BPA-PC is attributable to the bulky structure of the polymer,

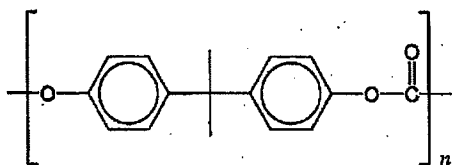


Fig. 1. Structure of BPA-PC.

which hinders segmental motion of the polymer chain. Unlike most amorphous polymers at temperatures below T_g , BPA-PC exhibits extraordinary impact strength and toughness. Its unusual low-temperature impact strength has been attributed by some authors to the presence of a low-temperature gamma transition that represents local scale motions of the polymer chain in the glassy state, which are thought to provide a mechanism for energy dissipation.^[29-32] Alternative theories incorporate the importance of free volume and residual stresses on PC impact behavior (recently reviewed in Ref.^[33]).^[33-35] As shown in Fig. 2, a low-temperature gamma transition temperature is observed at around -100°C . Additional transitions observed are the β transition at around 60°C and the α transition (T_g) at around 150°C . The β transition temperature is dependent on the thermal and mechanical history of the test sample and is attributed to residual stresses in the polymer sample as well as to the state of aging of the sample.^[36]

The mechanical, thermal, and processing parameters of PC depend on the molecular weight of the polymer. Typical commercial BPA-PCs for injection molding and extrusion applications have weight-average molecular weight (M_w) in the range of 17,000–36,000 as determined by light scattering. Molecular weight is often

approximated from the intrinsic viscosity using the Mark-Houwink-Sakurada relationship:

$$[\eta] = KM_v^a$$

where $[\eta]$ is the intrinsic viscosity, M_v is the viscosity-average molecular weight, and K and a are constants for a given polymer/solvent combination at a given temperature. Molecular weight, polydispersity index, intrinsic viscosity, and melt viscosity data have been correlated for a range of PCs of differing molecular weights.^[37] K and a values are reported for BPA-PC in a number of solvents.^[22,38-40] In general, mechanical and thermal properties such as impact resistance and softening point increase with increasing molecular weight, as does melt viscosity (and thus resistance to flow). Mechanical properties increase rapidly with increasing molecular weight at low molecular weights, but at molecular weights higher than around 22,000 (intrinsic viscosity approximately 0.45 dl/g), only slight changes are observed. Melt viscosities, however, continue to increase, making melt processing increasingly difficult. To optimize the balance of processability with mechanical properties, the PC of lowest molecular weight that meets minimum mechanical property requirements should be chosen for a given application. Higher-viscosity resins are typically used for extrusion applications, where high melt viscosities are tolerated and high strengths are required. Very low viscosity resins are used in applications such as injection molding of CDs, where high flow is necessary but impact strength is of secondary importance. Melt flow rates, intrinsic viscosities, and molecular weights for typical commercial BPA-PCs are given in Table 1.

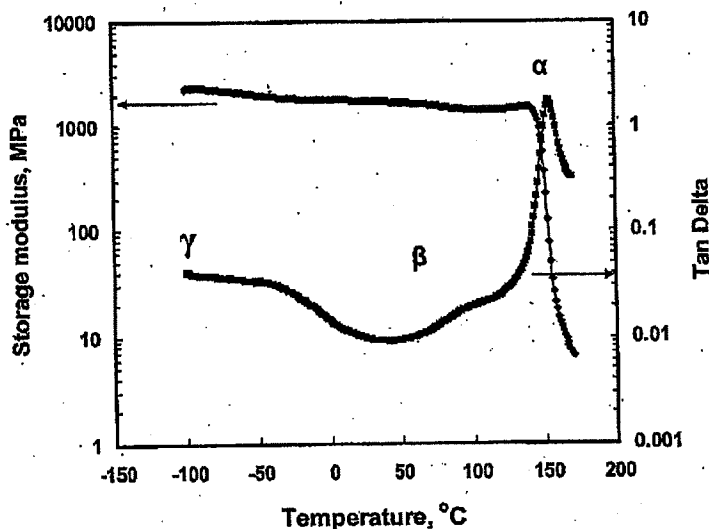


Fig. 2. Dynamic mechanical analysis data for LEXAN 101 PC resin. (Courtesy of GE.)

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